*Materials Science Forum*
*ISSN: 1662-9752, Vol. 907, pp 38-42*
*doi:10.4028/www.scientific.net/MSF.907.38*
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*Submitted: 2017-04-19*
*Revised: 2017-06-27*
*Accepted: 2017-07-13*
*Online: 2017-09-25*

# The Influence of Composition and Calcination Temperature on the Phases in $(Ba_{1-x}Sr_xZr)O_3$ Perovskites

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**Keywords:** barium strontium zirconate, cubic perovskite, microstructure, X-ray crystallography.

**Abstract.** Several ceramic materials with a perovskite structure often exhibit interesting electronic properties and, therefore, are often called "electroceramics". Electroceramics with high dielectric constants are used in capacitors and superconductors. The effect on calcination temperatures (1000°C–1400°C) and the changing of ions in A and B sites on the phase formation and microstructure of barium strontium zirconate $(Ba_{1-x}Sr_xZr)O_3$, BSZ, $x = 0.2$ and 0.4 ceramics were investigated. The BSZ powders were prepared using the solid state reaction method. The phase purity, crystal structure and microstructure of samples were examined using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD). We found out that the percentage phase purity of perovskite increases with an increase in the calcination temperatures as expected and it was found that BSZ powders adopts a perovskite structure with a cubic ($Pm\bar{3}m$) unit cell as well. The purity of perovskite powders was obtained above 1300°C and the purity phase of ceramics was detected in all samples.

## Introduction

Most of the useful ferroelectrics, such as barium titanate (BT), barium zirconium titanate (BZT), barium strontium zirconate (BSZ) and lead titanate ($PbTiO_3$), have the perovskite structure. Perovskite is the mineral name of calcium titanate ($CaTiO_3$) and its simplest structure is cubic, which is the high temperature form for many mixed oxides of the $ABO_3$ type. The simple cubic structure (space symmetry $Pm\bar{3}m$) consists of corner sharing oxygen octahedra ($BO_6$) arranged in three dimensions with smaller, highly charged cations ( B: $Ti^{+4}$, $Zr^{+4}$, $Sn^{+4}$, $Nb^{+5}$, $Ta^{+5}$, $W^{+6}$ etc.) located in the middle of the octahedra, and lower charged, larger cations (A: $Na^{+}$, $K^{+}$, $Ca^{+2}$, $Ba^{+2}$, $Pb^{+2}$, $Sr^{+2}$ etc.) in between the octahedra [1].

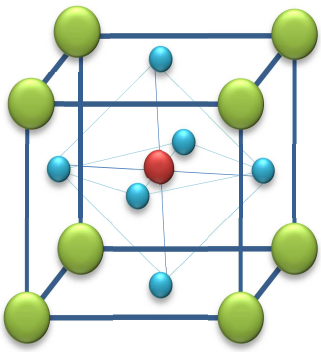


Fig. 1. Unit cell of a perovskite compound, $ABX_3$: A = green, B = red, X = blue

The structure is shown in $BaZrO_3$ has a cubic perovskite structure with a lattice constant of 4.193 Å and a high melting point of about 2600 °C (Fig.1). It is an important technological material and has found widespread applications in dielectrics, piezoelectrics, electro optic materials, catalysts and proton conductors [2-7]. In addition, $BaZrO_3$ has excellent thermal stability and resistance due to a low coefficient of thermal expansion (a = $87x10^{-7}$ / °C between 25°C and 1080°C) [9]. Few lectures reported to investigate the microstructure, production method and pure perovskite density of $BaZrO_3$ based ceramics. Kim et al. and Eitssayeam et al. were studied on been prepared by the sol-gel technique [9, 10] but this form of processing sample preparations is complex and expensive [11].

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Alternatively, the solid-state reaction method is probably one of the most fundamental, practical and routine methods which has been used, developed and modified in both scientific research and industrial mass production for many years [12,13]. Erb et al. [8] reported that in the case of solid-state powders, a heat treatment at 1700 °C for 48 h was needed to obtain samples with 98.5% of the theoretical density. In all the above cases, $BaZrO_3$ powder has been synthesized through the conventional solid state method which involves prolonged calcinations at high temperatures with intermediate grindings, yielding large coarse grained micron sized powders [14-16]. However, the effect of calcination temperature in Sr doped $BaZrO_3$ on the structure properties was not reported. In this present study, the phase formation, percentage pure perovskite phase and microstructure of $(Ba_{1-x}Sr_xZr)O_3$, BSZ, $x$ = 0.2 and 0.4 ceramic powders were investigated.

## Experimental Study

The compositions were prepared from $BaCO_3$, $ZrO_2$ and $SrCO_3$. All the chemicals were more than 99.5 % purity and from Alfa Aesar. Barium strontium zirconate $(Ba_{1-x}Sr_xZr)O_3$, (BSZ); $x$ = 0.2 and 0.4 powders were prepared via the solid-state reaction method by thoroughly grinding mixtures of the raw materials by a ball milling procedure (with zirconia balls milling under Isopropyl alcohol for 96h). Drying was carried out at 100°C for overnight. The mixing powders were calcined at temperatures ranging from 1000 to 1400°C, with a dwell time of 2h and a heating/cooling rate of 5°C/min. X-ray diffraction was employed to identify the phases formed and the optimum temperature for the pure crystal structure in the BSZ powders. The crystallite size was calculated from Full Width at Half Maximum (FWHM) using the Scherrer formula for the major (h k l) reflection of XRD patterns. The calcined powders morphologies were imaged using field emission scanning electron microscopy. The average particle sizes were determined by using a mean linear intercept method. Investigation of the molecular structure of the $(Ba_{1-x}Sr_xZr)O_3$ ceramic powders was carried out by fourier transform infrared spectroscopy (FTIR) using an AVATAR-320N spectrophotometer in the wave number range 400-3000 $cm^{-1}$ at room temperature.

## Results and Discussion

**X-ray Diffraction and FTIR Spectra.** Fig. 2a and Fig. 2b shows the XRD patterns of the BSZ powders of $x$ = 0.2 and $x$ = 0.4 with different calcination temperatures. They were indexed on the basis of a cubic structure matched with ICSD file number 74-1299. The impurity phases of BaO and $SrCO_3$, were observed when calcination temperatures were below 1300°C (see Fig. 2a) and all the impurity phases (BaO, $BaCO_3$, $SrCO_3$ and $ZrO_2$) were observed when calcination temperatures were below 1400°C (see Fig. 2b). The pure cubic perovskite phase was detected in powders calcined higher than 1400°C. The percentage of the perovskite phase was calculated with the equation (1), which is a well-known equation widely employed in connection with the preparation of complex perovskite structure materials [17]. Here *Iperov,* $I_{BaO}$, $I_{BaCO3}$, $I_{SrCO3}$ and $I_{ZrO2}$ refer to the intensity of the (101) perovskite peak, intensities of the highest BaO, $BaCO_3$, $SrCO_3$ peaks and $ZrO_2$, respectively.

$$\%_{Perovskite\ Phase} = \frac{I_{Perovskite}}{I_{Perovskite} + I_{BaO} + I_{BaCO_3} + I_{SrCO_3} + I_{ZrO_2}} \quad (1)$$

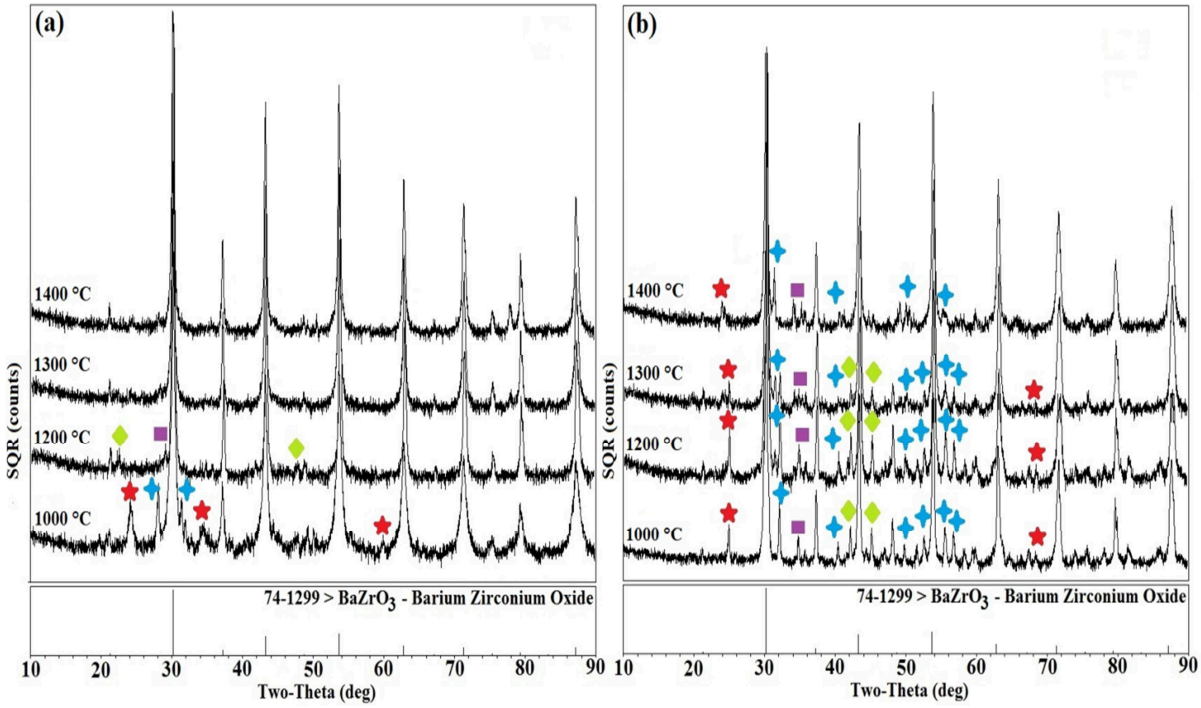



Fig. 2. (a) XRD patterns of $(Ba_{1-x}Sr_xZr)O_3$, x = 0.2 and (b) $x$ = 0.4 powders calcined at various temperatures for 2h. (★)$BaCO_3$, (■) BaO, (✦) $ZrO_2$, (◆) $SrCO_3$

The percent of the perovskite phase of BSZ calcined powders with $x$ = 0.2 and $x$ = 0.4 are listed in Table 1. An increase of phase purity with increasing calcination temperatures was evident. The highest percent perovskite phase of BSZ calcined powders with $x$ = 0.2 and 0.4 was obtained from the powder calcined at 1300°C and 1400°C respectively. Fig. 3a, 3b, 3c and 3d illustrate the SEM photographs of morphological changes in the calcined BSZT powders with $x$ = 0.2 and 0.4. In general, the particles are agglomerated and spherical in shape with variation in particle size. As calcination temperatures increased from 1000 to 1400°C, the increased average particle size was between 210 and 450 nm for $x$ = 0.2 and from 180 to 370 nm for $x$ = 0.4 as displayed in Table 1. In each condition of calcined temperature, the average particle size of the $x$ = 0.2 was slightly larger than the $x$ = 0.4.

Table 1. Percent perovskite phase and average particle size of BSZ calcined powders

| Calcined temperature (°C ) | $x$ = 0.2 | | $x$ = 0.4 | |
|---|---|---|---|---|
| | Percent perovskite phase (%) | Average particle size (nm) | Percent perovskite phase (%) | Average particle size (nm) |
| 1000 | 89.47 | 210 | 84 | 180 |
| 1200 | 97.42 | 285 | 88.2 | 240 |
| 1300 | 100 | 340 | 90.68 | 290 |
| 1400 | 100 | 450 | 91.82 | 370 |

Fig. 3 shows the FTIR spectra of the calcined $(Ba_{1-x}Sr_xZr)O_3$, $x$ = 0.2 - 0.4 powders. The large vibration band observed around 539 $cm^{-1}$ in the calcined powder is due to Zr–O vibration in the perovskite structure. The peaks near 860–869 $cm^{-1}$ may be assigned to the metal oxide bond between strontium and oxygen and the peaks shifted slightly to higher wave number side with increase in the Sr content. The medium peaks near 1080–1120 $cm^{-1}$ are due to symmetric C—O stretch. In the IR spectrum of the Sr doped $BaZrO_3$ powder, the vibration band observed at 1450 $cm^{-1}$ is attributed to the existence of carbonate $CO_3^{2-}$ groups in the nanopowder with small amounts of $BaCO_3$ [18,19]. The large vibration band appearing in the range 750-550 $cm^{-1}$ is due to Zr–O vibrations in the perovskite structure [19]. The maximum of this band is observed at 596 $cm^{-1}$. The small peaks around 2350 $cm^{-1}$ observed in each sample have been attributed to atmospheric

$CO_2$. The increase in the absorption peak shifts to higher energy end with increase in Sr content is expected from a harmonic oscillator model that has been used to stimulate the two body stretching mode.

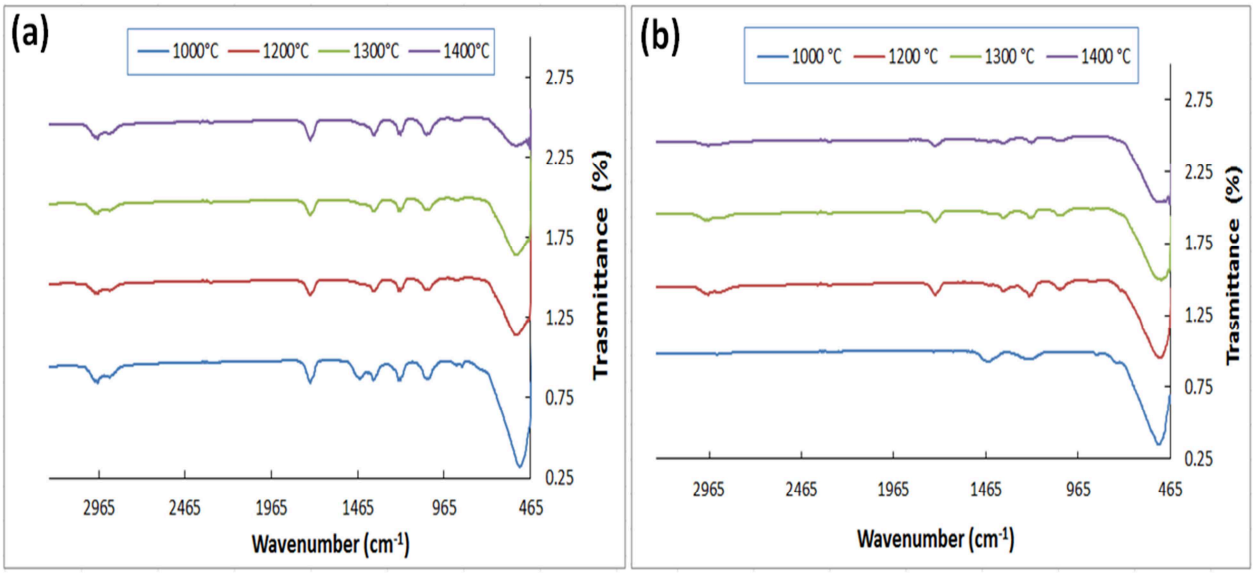



Fig. 3. FTIR spectra of calcined $(Ba_{1-x}Sr_xZr)O_3$, (a) $x = 0.2$ and (b) $x = 0.4$ powders

## Conclusions

The pure cubic crystal and the maximum percentage of the perovskite phase (91.8%-100%) of $(Ba_{1-x}Sr_xZr)O_3$ powders with $x = 0.2$ and $x = 0.4$ can be obtained by calcination at 1300 and 1400°C through the solid-state reaction method. The second phase found in BSZ powders with $x = 0.4$ disappeared in all sintered samples. BSZ ceramics in both compositions were identified as a single phase with a cubic perovskite structure. The average particle size and the average grain size increased with the increasing of calcination and sintering temperatures. The phase purity of Sr doped $BaZrO_3$ nanopowders has been confirmed using Fourier transform of infrared spectroscopy (FTIR). At calcination temperature of below 1300°C ($x = 0.2$) and below 1400°C ($x = 0.4$), the small amount of carbonate impurities still present in the samples as proven by FTIR and XRD results. The crystallization, lattice parameter and homogeneity of the calcined powders had been influenced by the calcinations, sintering temperatures and the change of ions in the A and B sites.

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